FUEL CELL OUTPUT MODULATION AND TEMPERATURE CONTROL

TECHNICAL FIELD

The subject matter disclosed herein pertains to output of fuel cells and temperature control of fuel cells.

BACKGROUND

Most fuel cells exhibit output and/or durability characteristics that depend heavily on temperature. For example, certain cells require a minimum operating temperature for an electrolyte to function properly while other cells degrade quickly when subject to temperature transients. Thus, substantial effort has been directed to temperature control of fuel cells. However, most temperature control schemes rely on heat exchange between a fuel cell and a heat exchange fluid. Such schemes inherently rely on heat transfer phenomena, which may introduce substantial time constants that make temperature control sluggish at best.

Consequently, a need exists for temperature control schemes that reduce lag times associated with heat transfer phenomena. In addition, as described herein, various exemplary arrangements and/or methods can provide for temperature control and/or control of fuel cell efficiency.

SUMMARY

An exemplary fuel cell system includes a first fuel cell capable of providing an electrical output; a second fuel cell capable of providing an electrical output; and a switch circuit that includes one or more switches for arranging the electrical output of the first fuel cell and the electrical output of the second fuel cell in parallel or series. Such a system may also include a temperature measurement circuit capable of measuring the temperature of the first fuel cell or the second fuel cell and providing a signal to the switch circuit. An exemplary method includes supplying an excess

amount of fuel to a multiple fuel cell system; switching at least some of the fuel cells from a parallel electrical arrangement to a series electrical arrangement; and producing heat from at least some of the excess amount of fuel. Another exemplary method includes supplying a substantially constant amount of fuel to a multiple fuel cell system; switching at least some of the fuel cells from a series electrical arrangement to a parallel electrical arrangement; increasing EMF efficiency; and reducing fuel efficiency. Various other exemplary fuel cell systems, arrangements, methods and controllers are also disclosed.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a diagrammatic illustration of a fuel cell.

Fig. 2 shows a plot of theoretical thermodynamic efficiency versus temperature for fuel utilization.

Fig. 3 shows a plot of cell EMF versus temperature for an exemplary fuel cell.

Fig. 4 shows a plot of cell EMF and power density versus current density from an exemplary fuel cell at a given temperature.

Fig. 5 shows a plot of EMF efficiency versus power density for an exemplary fuel cell at a given temperature.

Fig. 6 shows exemplary schematics of fuel cell systems.

Fig. 7 shows an exemplary switchable arrangement for a first and second fuel cell that supply power to a load.

Fig. 8 shows an exemplary switchable system that includes a controller and a plurality of fuel cells.

Fig. 9 show an exemplary method that includes switching an electrical arrangement of at least some fuel cells in a multiple fuel cell system.

DETAILED DESCRIPTION

The following Detailed Description discusses exemplary fuel cells, exemplary fuel cell electrical arrangements or configurations and exemplary controllers.

Various exemplary methods for operating or using such exemplary fuel cells, exemplary fuel cell arrangements or exemplary controllers are also discussed.

Fuel Cells

A fuel cell can generate electricity and heat by electrochemically reacting a fuel and an oxidizer using an ion conducting electrolyte for transfer of charged species without combustion. A typical fuel cell may generate an electrical potential through conversion of energy stored in a fuel (e.g., hydrogen, natural gas, methanol, etc.) and an oxidant (e.g., oxygen).

Fig. 1 shows a prior art solid oxide fuel cell 100. The fuel cell 100 includes an anode 110, a cathode 114 and an electrolyte 118. The anode 110 and the cathode 114 are electrodes while the electrolyte 118 serves as a type of membrane. In a typical operation of the fuel cell 100, an oxidant containing gas such as air is provided to the cathode 114, which may be referred to as an "air electrode", while a fuel is provided to the anode 110, which may be referred to as a "fuel electrode". For example, the cathode 114 may receive oxygen (from air) and the anode 110 may receive hydrogen (and optionally carbon monoxide, methane and other hydrocarbons). In this example, oxygen and hydrogen react to form water. This reaction is exothermic and it has an associated potential whereby the fuel cell 100 provides a flow path for electrons according to the potential.

Essential to operation of the fuel cell 100 is the electrolyte 118. As mentioned, the electrolyte 118 acts as a type of membrane, for example, an ion-conducting membrane. In the example given, the electrolyte 118 is an oxygen ion conducting membrane. If H_2 is used as a fuel, two protons or hydrogen ions are formed at the anode 110 from each H_2 molecule due to removal of electrons. An electron flow path or circuit 124 allows these electrons to become available at the cathode 114, which helps to drive oxygen ion formation from O_2. Oxygen ions conduct or permeate the electrolyte 118 and the anode 110, where the oxygen ions

form water with protons or hydrogen ions. The electrochemical process may be represented by the following reaction equations:

$$O_2 + 4e^- \rightarrow 2O^{2-}$$
$$2H_2 \rightarrow 4H^+ + 4e^-$$
$$4H^+ + 2O^{2-} \rightarrow 2H_2O$$

At a temperature of 25°C and a pressure of 1 ATM, a hydrogen-oxygen fuel cell according to the reaction equations has an equilibrium electromotive force (EMF) of approximately 1.2 V.

In general, an electrolyte should have a high transport rate for desired ionic species while preventing transport of unwanted species. Various ceramics (e.g., electroceramics) have properties suitable for use as electrolyte. For example, a group of electroceramics, referred to sometimes as "fast ion conductors", "rapid ion conductors" or "superionic conductors", may support high transport rates for desired ionic species. A commonly used ceramic for oxygen ion ion-conducting membranes is yttria stabilized zirconia (YSZ). For an YSZ electrolyte to provide sufficient oxygen ion conductivity, fairly high temperatures are required (e.g., typically greater than 700°C), even for a thin electrolyte (e.g., less than approximately 10 μm). Of course, numerous costs are associated with operation at such high temperatures. For example, high cost alloys (e.g., superalloys, etc.) may be required as a fuel cell housing thereby increasing cost substantially. Stresses at such operating temperatures may also degrade anodes, cathodes and/or electrolytes and thereby increase cost. For example, a cathode may have a coefficient of thermal expansion that differs from that of an electrolyte. In such a situation, substantial shear stresses may develop at the interface between the cathode and the electrolyte and cause microfractures of the cathode and/or the electrolyte which, in turn, may diminish interfacial contact area and/or the ability of the electrolyte to reject unwanted species.

Further, operating temperatures and/or temperature cycling may have a detrimental impact on anode, cathode and/or electrolyte characteristics. For example, one or more metal components in an anode may have a tendency to agglomerate above certain temperatures. Temperature and/or oxidation-reduction cycling may also promote agglomeration. Agglomeration is known to occur in Ni-YSZ cermet anodes of solid oxide fuel cells and to be generally related to factors such as current density and fuel utilization. For example, evenly distributed nickel particles are desirable to maximize the interface or three-phase-boundary (TPB) between an anode and an electrolyte. Agglomeration occurs throughout an anode and causes an increase in "particle size" and a reduction in evenness of particle distribution. These effects decrease effective TPB and thereby increase anode losses. Eventually, a disparate distribution may result that wholly compromises interparticle (or interagglomerate) conductivity.

An agglomerate may further degrade an electrode upon oxidation. Oxidation typically occurs during and after cooling (e.g., as a part of a fuel cell's operational cycling). In Ni-YSZ cermet anodes, Ni particles or agglomerates typically oxidize during and/or after cooling. Upon oxidation, the particles or agglomerates increase in size. After a few heating and cooling cycles particles or agglomerates may become large enough to exert significant forces (e.g., stress) on, in this example, the ceramic YSZ matrix. Thus, oxidation and/or agglomeration may degrade or break a matrix and render an electrode inoperable or prohibitively inefficient. Hence, as mentioned in the Background section, a need exists for better temperature control of fuel cells. In turn, better temperature control may help to minimize various detrimental effects associated with temperature cycling and/or other variations in operational temperature.

For a solid oxide fuel cell (SOFC), a ceramic and metal composite, sometimes referred to as a cermet, of nickel-YSZ may serve as an anode while Sr-

doped lanthanum manganite ($La_{1-x}Sr_xMnO_3$) may serve as a cathode. Of course various other materials may be used for the anode 110 or the cathode 114. To generate a reasonable voltage, a plurality of fuel cells may be grouped to form an array or "stack". In a stack, an interconnect is often used to join anodes and cathodes, for example, an interconnect that includes a doped lanthanum chromite (e.g., $La_{0.8}Ca_{0.2}CrO_3$). Of course other materials may be suitable.

It is to be understood that a fuel cell may be one of solid oxide fuel cells (SOFCs), proton conducting ceramic fuel cells, alkaline fuel cells, polymer electrolyte membranes (PEM) fuel cells, molten carbonate fuel cells, solid acid fuel cells, direct methanol PEM fuel cells and others (see, e.g., other examples below). Various exemplary fuel cells presented herein are solid oxide fuel cells.

An electrolyte may be formed from any suitable material. Various exemplary electrolytes as presented herein are at least one of oxygen ion conducting membrane electrolytes, proton conducting electrolytes, carbonate (CO_3^{2-}) conducting electrolytes, OH^- conducting electrolytes, hydride ion (H^-) conducting and mixtures thereof. Regarding hydride ion electrolyte fuel cells, advances have been as to a molten hydride electrolyte fuel cell.

Yet other exemplary electrolytes are at least one of cubic fluorite structure electrolytes, doped cubic fluorite electrolytes, proton-exchange polymer electrolytes, proton-exchange ceramic electrolytes, and mixtures thereof. Further, an exemplary electrolyte is at least one of yttria-stabilized zirconia, samarium doped-ceria, gadolinium doped-ceria, $La_aSr_bGa_cMg_dO_{3-\delta}$, and mixtures thereof, which may be particularly suited for use in solid oxide fuel cells.

Anode and cathode may be formed from any suitable material, as desired and/or necessitated by a particular end use. Various exemplary anodes and/or cathodes are at least one of metal(s), ceramic(s) and cermet(s). Some non-

limitative examples of metals which may be suitable for an anode include at least one of nickel, copper, platinum and mixtures thereof. Some non-limitative examples of ceramics which may be suitable for an anode include at least one of $Ce_xSm_yO_{2-\delta}$, $Ce_xGd_yO_{2-\delta}$, $La_xSr_yCr_zO_{3-\delta}$, and mixtures thereof. Some non-limitative examples of cermets which may be suitable for an anode include at least one of Ni-YSZ, Cu-YSZ, Ni-SDC, Ni-GDC, Cu-SDC, Cu-GDC, and mixtures thereof.

Some non-limitative examples of metals which may be suitable for a cathode include at least one of silver, platinum, ruthenium, rhodium and mixtures thereof. Some non-limitative examples of ceramics which may be suitable for a cathode include at least one of $Sm_xSr_yCoO_{3-\delta}$, $Ba_xLa_yCoO_{3-\delta}$, $Gd_xSr_yCoO_{3-\delta}$.

Efficiency and Cell Output

A theoretical thermodynamic efficiency (η_{Thermo}) of a fuel cell may be determined based on the ratio of Gibbs energy (Δg_f) to enthalpy of formation (Δh_f) of the supplied fuel:

$$\eta_{Thermo} = \Delta g_f / \Delta h_f \qquad (1).$$

For water as a product, enthalpy of formation may be given as a "higher heating value" (HHV) corresponding to liquid or as a "lower heating value" (LHV) corresponding to vapor (e.g., steam). The thermodynamic efficiency (η_{Thermo}) generally decreases with respect to an increase in temperature due to a temperature related decrease in the Gibbs free energy (e.g., due to temperature and entropy term of the free energy equation). Fig. 2 shows a plot 200 representative of the relationship between theoretical thermodynamic efficiency and temperature for hydrogen utilization.

A relationship exists between maximum EMF of a cell and maximum efficiency and hence a relationship exists between operating voltage and efficiency. For a hydrogen fuel, if all the energy in the hydrogen fuel (e.g., calorific value,

heating value, or enthalpy of formation), were transformed into electrical energy, then the EMF (e.g., open circuit voltage) would be given by:

$$EMF = - \Delta h_f / 2F \qquad (2),$$

wherein the factor "2" is the number electrons transferred and F is Faraday's constant (96,485 coulombs). Where HHV is used, EMF is approximately 1.48 V while if LHV is used, then EMF is approximately 1.25 V.

The actual EMF efficiency of a fuel cell may also be given in relation to an EMF value:

$$\eta_{Cell} = V_c/EMF(HHV \text{ or } LHV) \qquad (3).$$

In addition, a fuel cell may not use all fuel supplied to the cell. Therefore, a fuel utilization coefficient may be given as:

$$\mu_f = m_f(reacted) / m_f(supplied) \qquad (4),$$

wherein m_f is the mass of fuel reacted by the cell (numerator) or supplied to the cell (denominator). Hence, the total efficiency may be given as:

$$\eta_{Total} = \mu_f * \eta_{Cell} \qquad (5).$$

The total efficiency inherently depends on temperature due to the dependence of EMF on temperature, according to the theoretical thermodynamic efficiency. However, other temperature effects may be considered. For example, Fig. 3 shows a plot 300 of cell EMF versus temperature for an exemplary hydrogen fuel cell. Note that 100% efficiency is not achieved on either a LHV or HHV basis and that EMF decreases with respect to increasing temperature above approximately 500°C, wherein a suitable operational temperature range may exist from approximately 500°C to approximately 800°C or more.

Fig. 4 shows a plot 400 of cell EMF and power density versus current density for an exemplary fuel cell at a temperature of approximately 700°C. According to the data, cell EMF decreases with respect to an increase in current density. Power density is defined as current density multiplied by EMF; hence, power density exhibits a maximum with respect to current density. Further, any increase in temperature above 700°C (e.g., within a suitable operational range) will result in a

decrease in EMF and thus a decrease in power density. However, according to plot 300, a decrease in temperature below approximately 500°C, will result in a significant decrease in EMF and hence power density.

Fig. 5 shows a plot 500 of cell EMF efficiency versus power density for an exemplary fuel cell at a temperature of approximately 700°C. According to the plot 500 and the plot 400, as current density increases, cell EMF decreases and hence, cell EMF efficiency decreases. For example, if an EMF (LHV) of 1.15 V is assumed, then an efficiency of 80% would correspond to an EMF of approximately 0.9 V. From the plot 400, such a cell would be operating at a current density of approximately 0.36 Acm^{-2} and a power density of approximately 0.3 Wcm^{-2}. Consider another example where a cell is operating at an EMF efficiency of 60% or an EMF of approximately 0.7 V. According to the plot 400, an EMF of approximately 0.7 V corresponds to a current density of approximately 0.6 Acm^{-2}, which yields a power density of approximately 0.42 Wcm^{-2}. However, the same power density may be achieved using a different EMF efficiency as well. For example, an EMF efficiency of approximately 30% corresponds to an EMF of approximately 0.36 V and a current density of approximately 1.18 Acm^{-2}. Thus, assuming for ease of calculation, a cell having 1 cm^2, a load that requires a power of approximately 0.42 W can be powered by the cell operating at a high EMF efficiency state or a low EMF efficiency state. The high EMF efficiency state corresponds to a high EMF and a low current while the low EMF efficiency state corresponds to a low EMF and a high current. According to various cell arrangements discussed herein, a cell is optionally switched between a high EMF efficiency state and a low EMF efficiency state while maintaining a constant power output. Of course, at the low EMF efficiency state, more fuel is utilized or consumed when compared to the high EMF efficiency state. Table 1 below shows aforementioned operational conditions for an exemplary cell at two different states.

Table 1. Operational States

	State 1	State 2

EMF Efficiency	Low	High
EMF	Low	High
Current	High	Low
Power	Equal to State 2	Equal to State 1
Fuel Utilization	High	Low

Regarding fuel utilization, if a cell is supplied a constant amount of fuel, for example, according to a low EMF efficiency state (e.g., State 1) and then switched to a high EMF efficiency state (e.g., State 2), an excess supply of fuel will result. Hence, fuel efficiency, which is defined as amount of fuel reacted divided amount of fuel supplied, will decrease. However, if a cell is supplied a constant amount of fuel, for example, according to a high EMF efficiency state (e.g., State 2) and then switched to a low EMF efficiency state (e.g., State 1), fuel may become limiting, or alternatively, fuel efficiency will increase because the low state (e.g., State 1) utilizes more fuel than the high state (e.g. State 2). Thus, in general, for constant fuel supply, a switch from a low EMF efficiency state to a high EMF efficiency state results in excess fuel while a switch from a high EMF efficiency state to a low EMF efficiency state results in a decrease in excess fuel (e.g., perhaps even a limiting amount of fuel).

Exemplary Arrangements

As discussed above, a cell may operate at more than one state while maintaining a constant power output. In addition, cell EMF and current density are variable parameters that are related to fuel utilization, EMF efficiency, etc. An exemplary arrangement allows for at least some cells in multiple cell system to be switched between parallel and series electrical arrangements. First, various exemplary arrangements are described and then various methods of operating the exemplary arrangement are described that account for power and fuel considerations.

As described herein at least some cells in a multiple cell system are operated in series and/or parallel. When cells are electrically connected in series (e.g., a positive terminal of one cell connected to a negative terminal of another cell, etc.), the total voltage output of the cells is equal to the sum of the individual cell voltages. The current flow through a cell connected in series is the same as for a single cell. In contrast, when cells are connected in parallel (e.g., positive terminals connected together and negative terminals connected together), current capacity increases. The total voltage output of cells connected in parallel is the same as that of a single cell, assuming the cells have substantially equal voltage outputs. In essence, connecting cells in parallel has an effect somewhat analogous to increasing size of electrodes and electrolyte in a single cell.

Fig. 6 shows schematics 600 of two exemplary arrangements 610, 620. A parallel arrangement 610 includes a first cell operating at a temperature T_1 and producing an EMF V_1 and a second cell operating at a temperature T_2 and producing an EMF V_2 wherein V_1 equals V_2. A load, represented by a resistor has a resistance R_L. The temperature measuring circuits for the first cell and the second cell are optional. In the exemplary arrangement 610, the load experiences an EMF V_P that is equal to EMF V_1 and EMF V_2. Further, the arrangement produces a current I_P and a power P equal to the product of I_P and V_P. In the exemplary arrangement 610, each cell provides only part of the current I_P.

A series arrangement 620 includes a first cell operating at a temperature T_1' and producing an EMF V_1' and a second cell operating at a temperature T_2' and producing an EMF V_2' wherein V_1' may equal V_2'. A load, represented by a resistor has a resistance R_L, as in the parallel arrangement 610. The temperature measuring circuits for the first cell and the second cell are optional. In the exemplary arrangement 620, the load experiences an EMF V_P that is equal to EMF V_1' plus EMF V_2'. Further, the arrangement produces a current I_P and a power P equal to the product of I_P and V_P. In the exemplary arrangement 620, each cell provides a current I_P.

A comparison of the exemplary parallel arrangement 610 to the exemplary series arrangement 620, indicates that V_1' is less than V_P (as well as V_1 and V_2) and that V_2' is less than V_P (as well as V_1 and V_2). Further, in the exemplary parallel arrangement 610, the current demand I_P is distributed between the two cells whereas each cell in the exemplary arrangement 620 must supply the current demand I_P. Thus, given the load having resistance R_L and an EMF demand of V_P, the exemplary series arrangement 620 may be associated with a low EMF efficiency state of operation (low EMF, high current) when compared to the exemplary parallel arrangement 610 (high EMF, low current). Hence, an exemplary manner of switching from a high EMF efficiency state to a low EMF efficiency state includes switching from a parallel arrangement of cells to a series arrangement of cells.

Fig. 7 shows an exemplary switchable arrangement of cells 700. The exemplary arrangement 700 includes a load having a resistance R_L connected to a switchable circuit having two parallel switches SP_1, SP_2, one series switch S_s and two cells FC_1 and FC_2. Also shown are optional temperature measurement circuits T_1 for FC_1 and T_2 for FC_2. When switches SP_1, SP_2 are closed and switch S_s is open, then the circuit operates the cells in parallel whereas when switches SP_1, SP_2 are open and switch S_s is closed, the circuit operates the cells in series. Thus, an exemplary system includes a first fuel cell capable of providing an electrical output, a second fuel cell capable of providing an electrical output and a switch circuit that includes one or more switches for arranging the electrical output of the first fuel cell and the electrical output of the second fuel cell in parallel or series. As described further below, the optional temperature measurement circuits may aid in determining when to switch from parallel to series or from series to parallel. For example, if in a parallel arrangement with an excess fuel supply, T_1 and/or T_2 fall below a set temperature, then a switch to a series arrangement may act to increase heat production and hence temperature. In this example, a temperature measurement circuit may measure T_1 and/or T_2 and then provide a signal to the switch circuit. Of course, a controller may control the switch circuit and optionally receive a signal from a temperature measurement circuit or other circuits.

Of course, the exemplary arrangement or equivalents thereof may be replicated throughout a multiple cell system. For example, Fig. 8 shows an exemplary system 800 that includes a plurality of fuel cells 810 (e.g., FC_1, FC_2, . . . FC_N) and a controller 820. The controller 820 controls the electrical arrangement of the fuel cells 810 wherein some or all of the fuel cells are switchable from parallel to series electrical arrangements and from series to parallel electrical arrangements. For example, a first set of cells FC_1 and FC_4 may be operating in parallel at an EMF V_A while a second set of cells FC_2, FC_3, FC_5, FC_6, FC_7 and FC_8 are operating in series at an EMF V_B wherein V_A is substantially equal to V_B. Further, the first set and the second set may be electrically arranged in parallel to a load, which will experience an EMF V_A. If the first set of cells FC_1 and FC_4 are switched from parallel to series (e.g., while still in parallel with the second set of cells), then the EMF for cells FC_1 and FC_2 will decrease and the first set of cells will be shifted to a lower EMF efficiency.

Exemplary Methods

Various exemplary arrangements allow for enhanced operational control of a multiple fuel cell system. For example, Fig. 9 shows an exemplary method 900. The method 900 includes a supply block 910, wherein an excess amount of fuel is supplied to a multiple fuel cell system. Next, in a switch block 920, at least some of the cells are switched from a parallel to a series electrical arrangement. In general, switching maintains a constant power output to one or more loads. However, as described above, switching cells from a parallel to a series electrical arrangement can also switch the cells from a high EMF efficiency state to a low EMF efficiency state. Thus, in such circumstances, the exemplary method 900 includes a production block 930, wherein heat is produced from at least some of the excess fuel because the low EMF efficiency state associated with the cells switched from parallel to series requires more fuel (e.g., a higher fuel utilization). In essence, the switch increases the fuel efficiency for the switched cells, which was defined as amount of fuel reacted to amount of fuel supplied.

In general, the production of heat associated with the increase in fuel reacted or utilized causes an increase in temperature of the cells. Hence, referring again to the exemplary schematics 600 of Fig. 6, the exemplary method 900 would cause T_1' to be greater than T_1 and T_2' to be greater than T_2. Of course, once a certain temperature is achieved, the exemplary method 900 may switch the same cells and/or other cells in a multiple cell system from a series to a parallel electrical arrangement. Such a switch would decrease fuel utilization, assuming a constant supply of fuel, and thereby decrease heat production and hence temperature. Overall, such an exemplary method is suitable for controlling temperature of individual cells in a multiple cell system. For example, referring to the exemplary system 800 and the discussion of the first set of cells FC_1 and FC_4, a switch from parallel to series may aim to increase the temperature of cells FC_1 and FC_4.

Of course, other exemplary methods may adjust fuel supply in conjunction with switching at least some of cells in a multiple cell system from parallel to series or series to parallel electrical arrangements. Overall, switching as described herein, when combined with fuel supply considerations, provides a relatively quick and effective method for adjusting EMF efficiency and controlling temperature of at least some cells in a multiple cell system.